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VAPOR PRESSURE OF GD

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14. ABSTRACT

The vapor pressure of pinacolyl methyl phosphonofluoridate [O-(1,2,2-trimethylpropyl)-methyl phosphonofluoridate, GD] has been measured between -20 and 50 °C, using vapor saturation methodology. The current data are in good agreement with data previously measured.

15. SUBJECT TERMS

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PREFACE

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VAPOR PRESSURE OF GD

1. INTRODUCTION

The vapor pressure of GD has been measured previously using differential thermal analysis (DTA) between 68.5 and 190.2 °C (Laboratory Notebook No. 8343, p 92),[1] isoteniscope between 40 and 95.1 °C,[2] Knudsen effusion between -23.4 and 39.9 °C,[2] and vapor saturation between -35 and 0 °C.[3] An Antoine equation correlation, based on these data, has been published.[4]

Vapor pressure data for several CW agents and simulants have been measured in the ambient temperature range in our laboratory using a modified ASTM vapor saturation method.[5-9] We have also begun to assess the effect of ambient humidity on the volatility of simulants[10-13] and agents.[14] The current GD vapor pressure measurements have been performed using methodology most similar to that used recently for cyclohexyl methylphosphonofluoridate (GF)[7] and span the temperature range of 15 to 50 °C. Data have also been measured between -20 and 10 °C using the purge-and-trap method described in detail in an earlier report.[5]

The purpose of the present experiments was to lay the foundation for measuring the effect of humidity on GD volatility as a means to better understand its environmental behavior, as well as to confirm the validity of historical data, particularly in the ambient temperature range of interest.

2. EXPERIMENTAL PROCEDURES

The quantitative data reported herein were measured using a Hewlett Packard Model 5890 Series II gas chromatograph (GC) equipped with a flame ionization detector (FID). Nitrogen was used as the GC carrier at a flow rate of 8 (actual) cubic centimeters per minute (ccm) and was also used as the detector make-up gas at a flow rate of 22 ccm. The combustion gases were air (400 ccm) and hydrogen (30 ccm). The GC column used for the saturator purge-and-trap experiments was 30 m long, 0.53-mm inside diameter fused silica with 1.0 μm Rtx®-1 film thickness (Crossbond® 100% polydimethylsiloxane, Restek Corporation, Bellefonte, PA). The GC column for the saturator gas loop experiments was 15 m long, 0.53-mm inside diameter fused silica with 1.0 μm HP-1701 film thickness (14% cyanopropylphenyl - 86% methylpolysiloxane, Agilent Technologies, Wilmington, DE). The column used for the saturator purge-and-trap experiments was maintained at 40 °C for 1.5 min following sample introduction, then heated at a rate of 20 °C/min to 240 °C. Using the instrumentation and operating conditions described, GD eluted at 7.4 min, corresponding to a GC column temperature of 158 °C. The column used for the saturator gas loop experiments was heated at a rate of 15 °C/min from 40 °C to 160 °C. Using the instrumentation and operating conditions described, GD eluted at 3.9 min, corresponding to a GC column temperature of 98.5 °C.

All calibrations were performed by adding an accurately measured volume of analyte to the appropriate solvent to produce a solution of known concentration. A precisely measured volume of the calibration solution was injected and the resulting GC retention times and peak areas were measured. Calibration curves relating analyte mass and GC area were determined before and after measuring saturator data for GD using standard methodology.[5]

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The saturator methodology, used in this work to measure data between 15 and 50 °C, was identical to that used previously in this lab for measurement of GF vapor.[7] Data obtained between -20 and 10 °C were measured using saturator purge and trap methodology similar to that used previously for VX.[5] The reason that the two methods were required is the large dynamic range of the current data, making each unsuitable at one extreme.

The GD used for the present work was taken from CASARM Lot GD-U-2323-CTF-N. For the data measured between 15 and 50 °C, the GD used was assessed to be 98.8 ± 0.5% pure by acid-base titration (NIST-traceable through potassium acid phthalate #84f). For the data measured between -20 and 10 °C, the GD purity was assessed to be 96% by GC, thermal conductivity detection. Both samples were used without further purification. It is our assessment that the difference in purity is a result of the different analysis methods used and does not represent a degradation of the material. This issue is of minimal concern because the purity correction cancels in the data analysis. High-purity naphthalene (scintillation grade, 99+ %) was purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI) and used without further purification.

For the high-temperature data method, the sample loop volume was determined by calibrating the GC response for naphthalene and then using the known vapor pressure of naphthalene (15-22) to calculate loop volume as shown in Equation 1.

$$V_{loop} = n_{naphth} \cdot RT_{loop} / P_{naphth} \tag{1}$$

where

V_{loop} = sample loop volume

n_{naphth} = number of moles of naphthalene

R = gas constant ($8.314 \dfrac{Pa * m^3}{mole * K}$)

T_{loop} = sample loop temperature

P_{naphth} = vapor pressure of naphthalene

Measurements performed using this methodology at saturator temperatures of 25, 35, 45, and 50 °C resulted in a calculated loop volume of 1.12 ± 0.01 cc.

The vapor pressure of GD was determined as shown in Equation 2.

$$P_{GD} = n_{GD} \cdot RT_{loop} / V_{loop} \tag{2}$$

where

P_{GD} = vapor pressure of GD

n_{GD} = moles of GD

To confirm that the experimental system was operating under equilibrium conditions, the saturator flow rate was varied between 25 and 50 standard cubic centimeters per minute. No significant differences in GC area count were seen when the saturator flow rate was changed.

Data acquisition was controlled and recorded using National Instruments LabView® software and interfaces (SCXI 1001 chassis equipped with various 1320-series modules). Controlled parameters included the temperature of the saturator bath and saturator flow rate. Measured data included ambient pressure (for purge-and-trap data) and GC peak area. All of the controlled and measured data were captured and stored by the control program.

3.   RESULTS AND DISCUSSION

Belkin has reported GD vapor pressure data between 68.5 and 190.2 °C measured using DTA methods (Laboratory Notebook No. 8343, p 92).[1] Savage and Fielder reported GD vapor pressure data between -23.4 and 30 °C measured using Knudsen effusion and between 40 and 95.1 °C using an isoteniscope.[2] Table 1 lists the GD data measured in the present work using the gas saturation method. The Figure shows a plot of the GD vapor pressure data measured in the present work superimposed on the previous data listed in Tables 2-5. Previous attempts to measure sub-ambient vapor pressure data for GD were in substantial agreement with the accepted correlation for the two higher temperatures investigated but in rather poor agreement for the lower two data points as shown in Table 5. The Antoine equation used to calculate vapor pressures at the various temperatures was the same as given by Savage and Fielder and is given here in units appropriate for absolute temperature and Pascal:

$$\ln(P) = a - b/(c + T)$$

P= Pressure (Pascal)

a = 22.0945

b = 4382.05

c = -56.28

T = Temperature (K)

Vapor pressure data reported previously for GD using Knudsen effusion, isoteniscope, DTA, and saturator are listed in Tables 2-5, respectively. These tables reproduce the data in original units and significant figures used by the authors, because it was felt that it would be useful to collect all of these data into a single report and because the DTA data only exist in Belkin's notebook prior to this report. Calculated vapor pressure values based on the Antoine coefficients are presented in Table 6, along with heat of evaporation and volatility at each temperature.

4.   CONCLUSIONS

The current vapor pressure measurements for GD are in good agreement with those measured previously using three different methods.
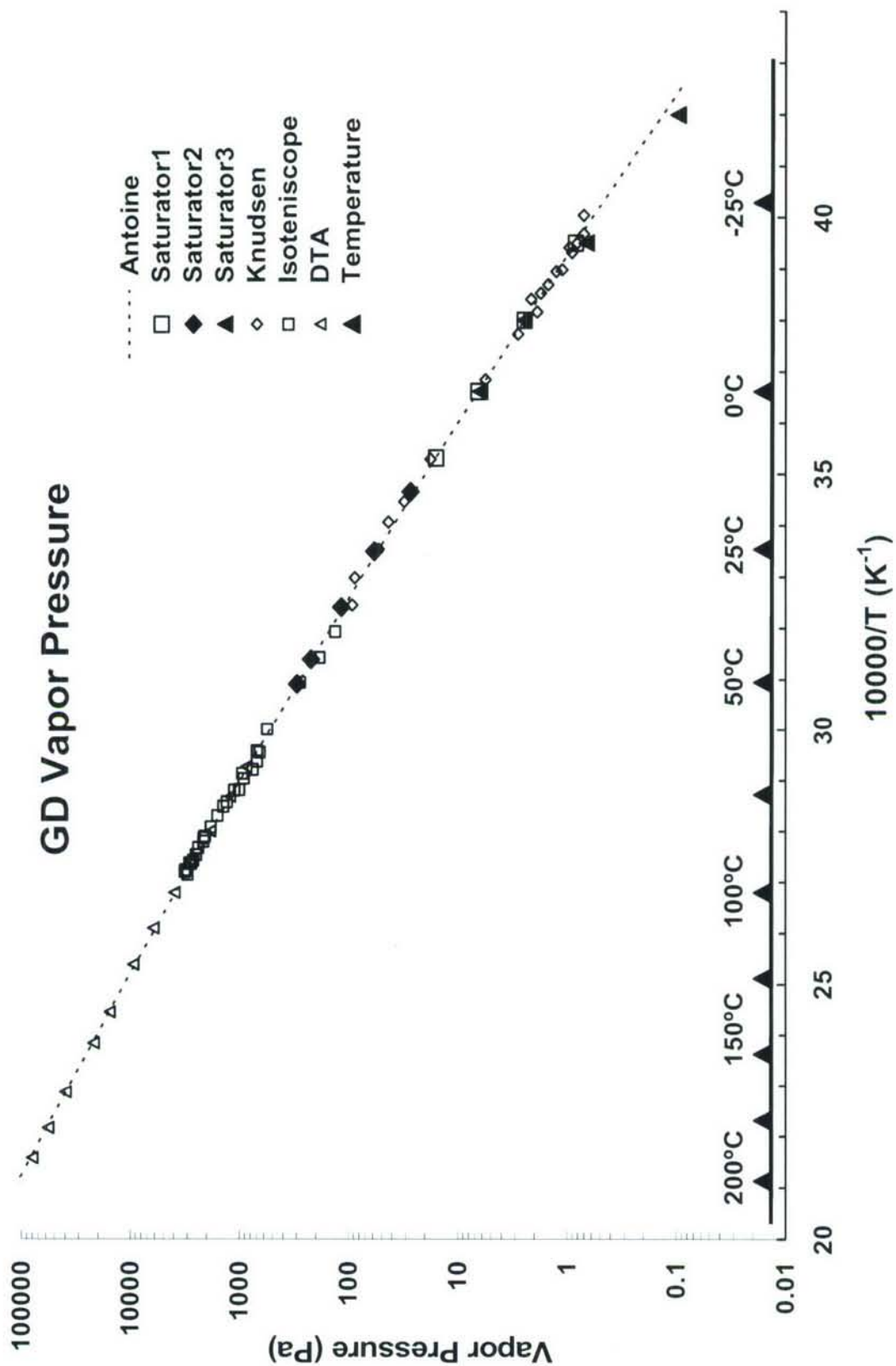
Figure. Vapor Pressure Data for Nerve Agent GD and Antoine Fit

Table 1. Vapor Pressure Measured in this Work for GD by Vapor Saturation using the Purge-and-Trap Method, -20 to +10 °C, and a Calibrated Sample Loop, +15 to +50 °C, Calculated Values using Antoine Equation from Savage and Fielder,[2] and Percent Difference

Temperature (°C)	Measured Vapor Pressure (Pa)	Calculated Vapor Pressure (Pa)	Percent Difference = 100 * (meas - calc)/calc
-20.0	0.835	0.8486	-1.6
-10.0	2.45	2.489	-1.6
0.0	6.53	6.610	-1.2
10.0	15.8	16.11	-1.9
15.2	27.2	25.24	7.6
25.2	58.2	54.98	5.9
35.3	117	112.6	4.2
45.4	223	218.4	2.1
50.4	299	298.5	0.2

Table 2. Literature Vapor Pressure Data Measured for GD using Knudsen Effusion by Savage and Fielder, Calculated Values using Savage's and Fielder's Antoine Fit Coefficients, and Percent Difference

Temperature (°C)	Measured VP (Torr)	Measured Vapor Pressure (Pa)	Calculated Vapor Pressure (Pa)	Percent Difference
-23.4	0.0053	0.707	0.5739	23.4
-21.1	0.0053	0.707	0.7489	-5.4
-20.0	0.0061	0.813	0.8486	-4.0
-19.4	0.0072	0.960	0.9080	6.0
-18.8	0.0068	0.907	0.9711	-6.4
-16.6	0.0084	1.12	1.238	-9.7
-16.4	0.0095	1.27	1.266	0.8
-14.7	0.0113	1.51	1.521	-0.7
-13.6	0.0132	1.76	1.710	2.9
-12.8	0.0162	2.16	1.861	16.1
-11.1	0.0142	1.89	2.222	-14.9
-10.2	0.0178	2.37	2.438	-2.5
-9.8	0.0182	2.43	2.540	-4.3
-8.1	0.0213	2.84	3.018	-5.6
-1.7	0.0423	5.64	5.635	0.2
10.2	0.1344	17.9	16.38	9.1
17.0	0.2336	31.1	28.71	8.4
20.4	0.3255	43.4	37.56	15.7
25.0	0.4000	53.3	53.36	0.0
30.0	0.6608	88.1	77.02	14.4
35.0*	0.7000	93.3	109.6	-14.8
39.9*	1.00	133	152.7	-12.8

*Reference 2 is ambiguous concerning these data points. Personal communication with J. Savage on 8 September 2006 indicated that they were performed using the Knudsen method.

Table 3. Literature Vapor Pressure Data Measured for GD using Isoteniscope by Savage and Fielder, Calculated Values using Savage's and Fielder's Antoine Fit Coefficients, and Percent Difference

Temperature (°C)	Measured VP (Torr)	Measured Vapor Pressure (Pa)	Calculated Vapor Pressure (Pa)	Percent Difference
40.0	1.00	133	153.7	-13.5
45.0	1.40	187	212.9	-12.2
50.0	2.10	280	291.3	-3.9
60.0	4.20	560	527.1	6.2
64.8	5.20	693	690.3	0.4
65.1	4.90	653	701.8	-7.0
67.2	5.20	693	787.2	-12.0
69.1	5.70	760	872.2	-12.9
70.0	7.10	947	915.1	3.5
71.2	6.90	920	975.3	-5.7
73.9	7.60	1013	1123	-9.8
74.0	8.40	1120	1129	-0.8
76.7	9.80	1307	1297	0.8
77.8	10.60	1413	1371	3.1
80.1	12.00	1600	1538	4.0
82.9	13.80	1840	1766	4.2
85.2	15.60	2080	1974	5.4
85.3	15.80	2106	1983	6.2
85.6	16.00	2133	2012	6.0
86.5	16.10	2146	2100	2.2
88.1	17.90	2386	2266	5.3
90.0	18.80	2506	2477	1.2
91.4	20.00	2666	2642	0.9
92.1	21.60	2880	2729	5.5
92.2	20.80	2773	2742	1.1
93.9	23.50	3133	2963	5.7
94.3	23.80	3173	3017	5.2
95.1	22.50	3000	3128	-4.1

Table 4. Vapor Pressure Data Measured for GD using DTA by Belkin and Brown, Values Calculated using Savage's and Fielder's Antoine Fit Coefficients, and Percent Difference between Calculated and Experimental Values

Temperature (°C)	Measured VP (Torr)	Measured Vapor Pressure (Pa)	Calculated Vapor Pressure (Pa)	Percent Difference
68.5	6.55	873.0	844.5	3.4
75.5	9.20	1227	1220	0.6
84.0	14.00	1867	1863	0.2
91.5	20.80	2773	2655	4.5
100.0	29.75	3966	3887	2.0
110.0	46.50	6199	5933	4.5
120.75	71.00	9466	9075	4.3
135.75	117.00	15599	15766	-1.1
146.25	165.00	21998	22585	-2.6
164.0	297.00	39597	39699	-0.3
178.0	430.00	57329	59696	-4.0
190.25	600.00	79993	83250	-3.9

Table 5. Vapor Pressure Data Measured for GD using Vapor Saturation by Podoll and Parish, Values Calculated using Savage's and Fielder's Antoine Fit Coefficients, and Percent Difference between Calculated and Experimental Values

Temperature (°C)	Measured VP (Torr)	Measured Vapor Pressure (Pa)	Calculated Vapor Pressure (Pa)	Percent Difference
-35	0.000723	0.0964	0.1353	-28.8
-20	0.00500	0.667	0.8486	-21.4
-10	0.0186	2.48	2.489	-0.4
0	0.0473	6.31	6.610	-4.6

Table 6. Vapor Pressure, Heat of Vaporization and Volatility of GD between –30 and 200 °C Calculated using Savage's and Fielder's Antoine Coefficients. Entries in bold are extrapolated beyond the range of measured data.

Temperature (°C)	Calculated Vapor Pressure (Pa)	ΔH_{vap} (kJ/mol)	Volatility (mg/m^3)
-30	0.2579	61.7	17.87
-20	0.8486	60.2	56.48
-10	2.489	59.0	159.4
0	6.610	57.8	407.7
10	16.11	56.8	958.4
15	24.43	56.3	1428.4
20	36.40	55.8	2092.3
25	53.36	55.4	3015.5
30	77.02	54.9	4280.6
35	109.5	54.5	5990.0
40	153.7	54.2	8270.2
45	212.9	53.8	11274
50	291.3	53.4	15187
55	394.0	53.1	20229
60	527.1	52.8	26657
70	915.1	52.1	44934
80	1531	51.6	73041
90	2477	51.0	114900
100	3887	50.5	175490
120	8834	49.6	378580
140	18310	48.8	746810
160	35140	48.1	1366700
180	63130	47.5	2347200
197.8	101325	47.0	3625300
200	107200	46.9	3818200

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